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Specification and Drawings, as originally filed, with Application for Patent Serial No:  
2,254,315, on November 20, 1998, by BAYER INC., assignee of Ahti August Koski, for  
"Process for Treating Particles, and Their Use in Dispersions".

  
Agent certificateur/Certifying Officer

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**ABSTRACT OF THE DISCLOSURE**

Particles are hydrophobicized by in situ formation of a moiety containing amino and silane groups. The invention is particularly useful for treating hydrophilic inorganic particles to provide the functionality of a coupling agent without the need to react the hydrophilic inorganic particles with a coupling agent, per se. The treated particles can be used, for example, as a compounding agent for polymers.

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PROCESS FOR TREATING PARTICLES, AND THEIR USE IN DISPERSIONS

In one of its aspects, the present invention relates to treating particles, particularly inorganic water-insoluble compounds. The treated particles are useful particularly, but not exclusively in the compounding of polymers, especially rubbers and plastics.

It is known in the art to utilize sulfur-containing organosilicon compound in a variety of rubber products in the last 25 years. Such known uses include tire walls and bodies, rubber hoses, rubber belts and numerous other rubber products.

Depending on the formulation, selected properties of the rubber can be modified.

Since the early 1980's, automobile manufacturers have been encouraging the production of low rolling-resistance tires. A number of sulfur-containing organosilicon compounds have been identified as useful in this regard. The improvements achieved include meeting fuel economy standards set in various countries with minimal or no sacrifice in wet traction and wear. Many of these sulfur-containing organosilicon compounds became known in the industry as coupling agents.

Examples of known coupling agents include those described in United States patent 4,704,414, published European patent application 0,670,347A1 and published German patent application 4435311A1.

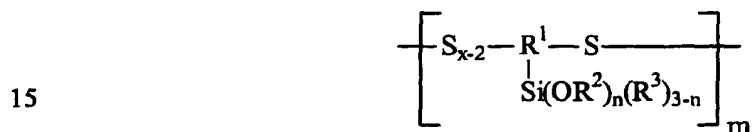
One suitable coupling agent is a mixture of bis[3-(triethoxysilyl)propyl]monosulfane, bis[3-(triethoxysilyl)propyl]disulfane, bis[3-(triethoxysilyl)propyl]trisulfane and bis[3-(triethoxysilyl)propyl]tetrasulfane and higher sulfane homologues - for example, coupling agents available under the trade names Si-69 (average sulfane 3.5) and Silquest™ A-1589 or Si-75 (average sulfane 2.0). In the past, achieving a good balance between the coupling agent and particles, such as silica, without scorching or premature curing has proven difficult.

Illustrative examples of other coupling agents include the following:

bis[(trimethoxysilyl)propyl]disulfane (Si-166), bis[(triethoxysilyl)propyl]disulfane (Si-266), bis[2-(trimethoxysilyl)ethyl]tetrasulfane, bis[2-(triethoxysilyl)ethyl]trisulfane, bis[3-(trimethoxysilyl)propyl]disulfane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldiethoxysilane, 3-mercaptoethylpropyl-

ethoxymethoxysilane, 1,3-bis(3-acryloxypropyl)tetramethoxydisiloxane,  
 acryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane,  
 allyltrimethoxysilane, diallyldiethoxysilane, 5-(bicycloheptenyl)triethoxysilane, 5-  
 (bicycloheptenyl)methylmethoxyethoxysilane, isopropoxytriacryltitanate,  
 5 diisopropyldimethacryltitanate, diethoxydi(3-mercaptopropoxy)zirconate,  
 triisopropoxy-(2-mercaptopropoxy)zirconate, and di[neopentyl(diallyl)oxy]-di(3-  
 mercaptopropoxy)-zirconate.

Other known coupling agents include those disclosed in published German  
 patent application 4435311A1 mentioned above. On pages 2 and 3 of this reference,  
 10 there is disclosure of oligomers and polymers of sulphur containing organooxysilanes  
 of the general formula:

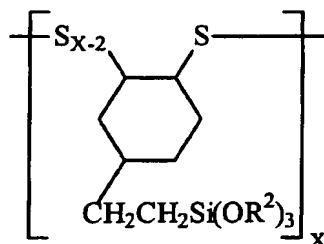


in which  $\text{R}^1$  is a saturated or unsaturated, branched or unbranched, substituted or  
 unsubstituted hydrocarbon group that is at least trivalent and has from 2 to 20 carbon  
 20 atoms, provided that there are at least two carbon-sulphur bonds,  $\text{R}^2$  and  $\text{R}^3$ ,  
 independently of each other, are saturated or unsaturated, branched or unbranched,  
 substituted or unsubstituted hydrocarbon groups with 1 to 20 carbon atoms, halogen,  
 hydroxy or hydrogen,  $n$  is 1 to 3,  $m$  is 1 to 1000,  $p$  is 1 to 5,  $q$  is 1 to 3 and  $x$  is 1 to 8.

Other coupling agents are of the general formula:

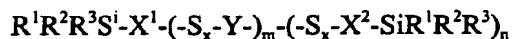
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wherein  $R^2$ ,  $m$  and  $x$  have the meanings given above.

Other known coupling agents include those of the general formula:



in which  $R^1$ ,  $R^2$  and  $R^3$  are the same or different and are  $C_{1-8}$  alkyl,  $C_{1-8}$  alkoxy, phenyl or phenoxy, provided that at least one of  $R^1$ ,  $R^2$  and  $R^3$  is an alkoxy or phenoxy group.  $X^1$  and  $X^2$  are the same or different and are divalent linear or branched, optionally unsaturated  $C_{1-12}$  alkyl groups,  $Y$  is a di-, tri- or tetravalent linear, branched or cyclic  $C_{1-18}$  alkyl group that is optionally unsaturated and is optionally substituted by  $C_{6-12}$  aryl,  $C_{1-8}$  alkoxy or hydroxy groups and which can be interrupted by oxygen, sulphur or nitrogen atoms or aromatic  $C_{6-12}$  aryl groups, or  $Y$  is a  $C_{6-12}$  aryl or heteroaryl group,  $m$  is an integer from 1 to 20,  $n$  is an integer from 1 to 6 and  $x$  is an integer from 1 to 6.

Alternatively, it is known in the art to produce "pre-treated" silica material which has been produced by reacting untreated silica with a coupling agent. Such material is available commercially under the tradename Ciptane™ (PPG) and Coupsil™ 8i13 (Degussa AG).

The prior art use of coupling agents is characterized by reacting the coupling agent with the particles of interest. In other words, the coupling agent is independently produced and thereafter reacted with the particles of interest.

While this approach has been satisfactory in the past, the expense of the coupling agent (usually obtained from an independent source) is relatively large.

Thus, there is an ongoing need for an approach of treating the particles of interest to obtain the benefits of the coupling agent while minimizing the expense associated with conventional coupling agents.

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### SUMMARY OF THE INVENTION

It is an object of the present invention to obviate or mitigate at least one of the above-mentioned disadvantages of the prior art.

Accordingly, in one of its aspects, the present invention provides a process for treating particles, the process comprising the step of:

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contacting a particulate material having Formula II:



(II)

wherein P is a particle, R is a hydrocarbylsiloxyl moiety and X is an anion, with a sulfur-containing compound to produce a particulate material having one or more of the formulae:

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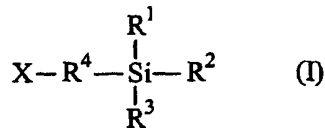
wherein n is an integer from 1 to 10.

In another of its aspects, the present invention provides a process for treating particles, the process comprising the steps of:

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(i) contacting a particulate material with a compound of Formula I:

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in which:

at least one of  $R^1$ ,  $R^2$  and  $R^3$  are hydroxyl or hydrolysable groups;  
 $R^4$  is a divalent group that is resistant to hydrolysis at the Si- $R^4$  bond; and  
X is an anion; and

5 (ii) contacting the particulate material with a sulfur-containing compound.

Thus, the present inventor has developed a novel approach for introducing the functionality of a coupling agent into a particulate material. Specifically, the present approach does not necessitate the production of a coupling agent, *per se*. Rather, the approach taught herein relates to *in situ* production of the functional moiety of the  
10 coupling agent on the particulate material (i.e., as opposed to reaction of the pre-manufactured coupling agent and the particulate material). One of the advantages of this approach is that relatively low cost chemicals can be used to produce the functional moiety of the coupling agent compared to the cost of the independently produced coupling agent, *per se*.

15 Preferably, the present process of treating a particulate material is carried out in an aqueous solution, suspension or slurry, so that the product of the process is an aqueous suspension or slurry of treated particles.

In one preferred embodiment, the suspension or slurry resulting from the present process, and containing the treated particles, is then mixed with a hydrocarbon  
20 solution of a polymer, and then dried to form a polymer-particle dispersion. This preferred embodiment results in the production of a dispersion comprising the polymer and the treated particles. In this embodiment, the treated particles may be incorporated into a suspension without being isolated (i.e., separated from the suspension or slurry, and subsequently dried). This preferred embodiment results in  
25 the production of a dispersion comprising a polymer and a treated particulate material (such as metal oxides and the like as will be discussed in more detail hereinbelow), the dispersion having been prepared from a polymer solution without the need to utilize conventional coupling agents, *per se*.

Alternatively, the treated particulate material may be separated from the  
30 suspension or slurry, and subsequently dried for later use (i.e., before addition of the polymer solution).

In this specification, the terms "concentrate", "dispersion" and "pre-dispersion", when used in the context of the present invention, are intended to mean a composition comprising a particulate material (i.e., the additive(s) to be used for compounding purposes) and a binder therefor, wherein the particulate material is the major component of the composition - i.e., the composition comprises at least about 50 percent by weight particulate material. Preferably, the composition comprises from about 50 to about 95, more preferably from about 60 to about 95, even more preferably from about 70 to about 95, percent by weight particulate material. In this specification, the term "masterbatch", when used in the context of the present invention, is intended to mean a composition comprising a particulate material (i.e., the additive(s) to be used for compounding purposes) and a binder therefor, wherein the particulate material is the minor component of the composition - i.e., the composition comprises less than about 50 percent by weight particulate material. Preferably, the composition comprises from about 5 to about 50, more preferably from about 20 to about 45, even more preferably from about 30 to about 40, percent by weight particulate material.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Embodiments of the present invention will be described with reference to the accompanying drawing, in which:

Figure 1 illustrates an example of the use of a conventional coupling agent; and

Figure 2 illustrates an example of an embodiment of the present process.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

With reference to Figure 1, there is illustrated the use of a conventional coupling agent. The coupling agent illustrated is a mixture of bis[3-(triethoxysilyl)propyl]monosulfane, bis[3-(triethoxysilyl)propyl]disulfane, bis[3-(triethoxysilyl)propyl]trisulfane and bis[3-(triethoxysilyl)propyl]tetrasulfane and higher sulfane homologues, the mixture having an average sulfane content of 3.5 (i.e., in Figure 1, the average value for n is 3.5). Such a coupling agent is available under the trade names Si-69. Thus, as illustrated, the alkoxy groups on one end of the coupling agent



react with the pendant hydroxyl groups on a first silica particle to form a series of siloxyl linkages to the first silica particle. Further, the alkoxy groups on the other end of the coupling agent react with the pendant hydroxyl groups on a silica particle to form a series of siloxyl linkages to the second silica particle. In this fashion, the first and second silica particles are "coupled" to one another. Of course, it is possible for opposed ends of the coupling agent to form siloxyl linkages with the same silica particles.

In one of its embodiments, the present process comprises the step of:  
contacting a particulate material having Formula II:

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wherein P is a particle, R is a hydrocarbylsiloxyl moiety and X is an anion, with a sulfur-containing compound to produce a particulate material having one or more of the formulae:

15



20

wherein n is an integer from 1 to 10, preferably from 2 to 5.

Throughout this specification, reference is made to silica as the particle having surface hydroxyl groups since this is the preferred particulate material, but it should be appreciated that the invention applies to the use of other such minerals, and the description understood accordingly. For example, carbon black may also be used. Further carbon-silica dual phase fillers may also be used (e.g., Ecoblack CRX-2000™).

Thus, the present process is particularly useful in the treatment of inorganic water insoluble compounds. Preferably, the inorganic water insoluble compounds useful for treatment are those such compounds which contain oxygen, more preferably such compounds which also contain a metal. Preferably, the metal is selected from Groups II-VIII of the Periodic Table of Elements. Examples of suitable groups of

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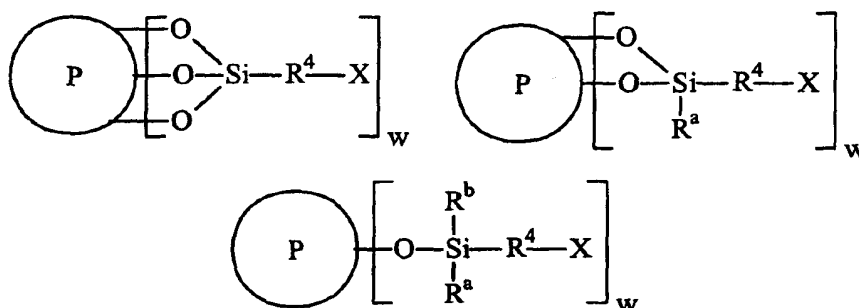
useful metal compounds may be selected from the group comprising oxides, hydroxides, borates, sulfates, carbonates, silicates, phosphates, chromates and the like.

Non-limiting examples of suitable metal compounds may be selected from the group comprising titanium oxide, ferric oxide, hydrated ferric oxide, ferrous oxide, antimony oxide, barium carbonate, zinc oxide, zinc borate, lead oxide (including red lead oxide), dibasic lead phosphite, lead silicate, tribasic lead sulfate and mixtures thereof.

Other suitable metal compounds, especially those which are water insoluble or only slightly soluble in water, will be readily apparent to those of skill in the art base on the foregoing discussion. For example, a particularly preferred application of the present invention is to hydrophobicize colorant or pigment particles which are typically used in the plastics industry. Non-limiting examples of suitable such particles may be selected from the group consisting of  $\alpha$ -FeOOH (goethite),  $\gamma$ -FeOOH (lepidocrocite),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite),  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) and Fe<sub>3</sub>O<sub>4</sub>.

As stated above, the preferred particulate material for use herein is silica.

Preferably, the particles of Formula II are selected from the group comprising:



wherein:

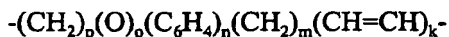
$\text{R}^4$  is a divalent group that is resistant to hydrolysis at the Si- $\text{R}^4$  bond;

$\text{R}^a$  and  $\text{R}^b$  are the same or different and each is selected from the group comprising hydroxyl, a hydrolysable group, C<sub>1-40</sub> alkyl, C<sub>2-40</sub> mono- or diunsaturated alkenyl and C<sub>5-40</sub> aromatic;

w is an integer in range of 1 to  $10^6$  or more. As will be appreciated by those of skill in the art the value of w depends, at least in part, on the size of the particle and the number of pendent reactive moieties.

Preferably,  $R^4$  has the formula:

5



wherein the order of the moieties is not restricted and

k is 0 or 1,

10

m is a whole number in the range 0 to 20,

n is 0, 1 or 2,

o is 0 or 1, and

p is a whole number in the range 0 to 20,

with the provisos that: (i) the sum of the values of k, m, n, o and p is at least 1 and not more than 20, and (ii) if o is 1, p is 1 or greater and the sum of k, m and n is 1 or greater. More preferably, n, o and p are all 0. Most preferably,  $R^4$  is  $-CH_2CH_2CH_2-$ .

Preferably, in the particles of Formula II, X is selected from the group comprising acetate, chloride, bromide, iodide and sulphate, more preferably from the group comprising chloride and bromide.

The present process involves the use of a sulfur-containing compound. As used throughout this specification, the term "sulfur-containing compound" is intended to encompass any compound capable of reaction with the particles of Formula II to leave the sulfane residue in the particulate material having the Formula III, wherein n is an integer of from 1 to 10. Preferably, the sulfur-containing compound has the formula  $M_yS_n$ , where M is ammonium or a metal, y is an integer which specifies the valency of M and n is an integer of from 1 to 10.

Generally, it is preferred that the sulfur-containing compound is selected from the group comprising sulfides, thiosulfates and mixtures thereof. More preferably, the sulfides comprise ammonium sulfide compounds and alkali metal sulfide compounds. Non-limiting examples of suitable alkali metal sulfides may be selected from the group comprising  $Na_2S_n$ ,  $K_2S_n$  and mixtures thereof, wherein n is as defined above.

More preferably, the thiosulfates comprise ammonium thiosulfate compounds and alkali metal thiosulfate compounds. Non-limiting examples of suitable alkali metal thiosulfate compounds may be selected from the group comprising  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{K}_2\text{S}_2\text{O}_3$  and mixtures thereof. The most preferred sulfur-containing compound for use in the present process is  $\text{Na}_2\text{S}_n$  wherein n is as defined above. It will be clearly apparent to those of skill in the art that mixtures of the same type of sulfur-containing compound may be used. Thus, for example, when  $\text{Na}_2\text{S}_n$  is used as the sulfur-containing compound, a mixture comprising two or more of  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{S}_2$ ,  $\text{Na}_2\text{S}_3$ ,  $\text{Na}_2\text{S}_4$ , etc. may be used to provide a desired overall average sulfane content - e.g., in the range of 2-5.

Other non-limiting examples of suitable sulfur-containing compounds include ammonium hydrogen sulfide ( $\text{NH}_4\text{SH}$ ) and alkali metal hydrogen sulfide compounds. Non-limiting examples of suitable alkali metal hydrogen sulfide compounds may be selected from the group comprising  $\text{NaSH}$ ,  $\text{KSH}$  and mixtures thereof. The use of these hydrogen sulfide compounds will result in production of a treated particulate material having the general formula



It is preferred to utilize the sulfur-containing compound in the form of an aqueous solution thereof. Preferably, the sulfur-containing compound is present in a concentration in range of from about 20% to about 50%, more preferably from about 25% to about 40%, most preferably from about 30% to about 40%, by weight of the aqueous solvent. Other organic solvents for the sulfur-containing compounds may be used although these are less preferred.

In a preferred embodiment, the treatment is carried out in an aqueous dispersion or slurry of the particles. Generally, the precise make up of the slurry is not particularly restricted provided that it is a mobile suspension. Practically, it is preferred that the slurry contain up to about 60% by weight, more preferably up to about 50% by weight, of particles to be treated. While the physical nature of the particles to be treated is not particularly restricted, it is preferred that they have an average particle size in the range of from about 0.1  $\mu\text{m}$  to about 100  $\mu\text{m}$ , preferably from about 10  $\mu\text{m}$  to about 50  $\mu\text{m}$ , most preferably from about 10  $\mu\text{m}$  to about 25  $\mu\text{m}$ .

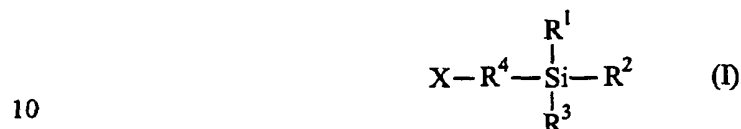
In the preferred embodiment, the treatment is carried out in an aqueous dispersion or slurry and the concentration of the aqueous dispersion or slurry of silica particles may be between 1 and 30 percent by weight of silica in water, preferably between 5 and 25 percent by weight of silica in water and most preferably between 8 and 22 percent by weight of silica in water. Dried amorphous silica suitable for use in accordance with the invention may have a mean agglomerate particle size between 1 and 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of between 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/II, of from 0 to 10 percent by weight. If filter cake is used, it may be made by any known means such as described in Ullmann's Encyclopedia of Industrial Chemical Vol A23 pages 642-643, VCH Publishers, ©1993. The filter cake has a preferred solids content of between 5 and 30 percent by weight, most preferably between 15 and 25 percent by weight, and it may be redispersed in water in accordance with the present process to give a silica concentration of between 5 and 20 percent by weight and most preferably between 8 and 12 percent by weight. It is preferred to use a filter cake.

If a never-filtered slurry prepared from the known reaction of a solution of alkali metal silicate with either mineral acid or carbon dioxide is used, it is preferred that the solids content of the never-filtered slurry be between 1 and 30, more preferably between 5 and 10, percent by weight of silica. The slurry temperature may be between 0° and 100°C if the process is conducted at atmospheric pressure or between 0° and 135°C if the operation is conducted in a pressure vessel. Most preferably, the process is conducted at atmospheric pressure in which case the preferred temperature is between 30° and 95°C and most preferably between 45° and 90°C.

The reaction between the particles of Formula II and the sulfur-containing compound is conducted for a period sufficient to achieve a chemical reaction between

the two reactants. Generally, the time needed will depend on factors such as the reaction temperature, the parameter X in Formula II and the like, all of which are readily determined and controllable by those of skill in the art.

- In a preferred embodiment of the present process, the particles of Formula II  
 5 are prepared by a process comprising the step of:  
     contacting a particulate material with a compound of Formula I:



in which:

- at least one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are hydroxyl or hydrolysable groups; and  
 15 X and R<sup>4</sup> are as defined above.

It is desirable that, prior to the addition to the silica particles of the compound of Formula I, the dispersion or slurry shall have a pH in the range from 6 to about 8, more preferably from about 6.8 to about 7.2. If necessary, the pH can be adjusted by addition of acid or alkali, for example mineral acid, alkali metal hydroxide, alkaline  
 20 earth hydroxide, ammonium hydroxide and the like. These can be added as such or in aqueous solution.

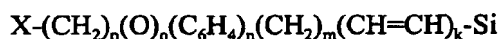
In the compound of Formula I, it is preferred that at least two, most preferably all three, of the groups R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are readily hydrolysable. Suitable groups R<sup>1</sup> include hydroxyl groups and hydrolysable groups of formula OC<sub>p</sub>H<sub>2p+1</sub>, where p has a  
 25 value from 1 to 10. The alkyl chain can be interrupted by oxygen atoms, to give groups, for example, of formula CH<sub>3</sub>OCH<sub>2</sub>O-, CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>2</sub>O-, CH<sub>3</sub>(OCH<sub>2</sub>)<sub>4</sub>O-, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O-, C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>O-, C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>OCH<sub>2</sub>O-, or C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>O-. Other suitable hydrolysable groups include phenoxy, acetoxy, chloro, bromo, iodo, ONa, OLi, OK or amino or mono- or dialkylamino, wherein the alkyl group(s) have 1 to 30  
 30 carbon atoms.

$R^2$  and  $R^3$  can take the same values as  $R^1$ , provided that only one of  $R^1$ ,  $R^2$  and  $R^3$  is chloro, bromo or iodo. Preferably, only one or two of  $R^1$ ,  $R^2$  and  $R^3$  is hydroxyl or ONa, OLi or OK.

Non-limiting examples of groups  $R^2$  and  $R^3$  that are not hydrolysable include  
 5  $C_{1-40}$  alkyl,  $C_{2-40}$  mono- or diunsaturated alkenyl and  $C_{5-40}$  aromatic, preferably  $C_{1-10}$  alkyl,  $C_{2-10}$  mono- or diunsaturated alkenyl and phenyl.  $R^2$  and  $R^3$  can also each be a group  $-R^4-NR^5R^6$ , discussed further below. It is preferred that  $R^1$ ,  $R^2$  and  $R^3$  are all the same and are  $CH_3O-$ ,  $C_2H_5O-$  or  $C_3H_8O-$ . Most preferably they are all  $CH_3O-$ .

The divalent group  $R^4$  is preferably such that  $X-R^4-Si$  is of the formula:

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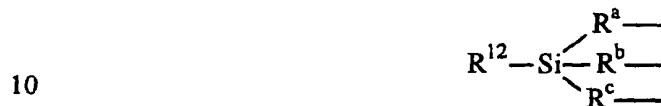


in which  $k$ ,  $m$ ,  $n$ ,  $o$  and  $p$  are all whole numbers. The order of the moieties between  $N$  and  $Si$  is not particularly restricted other than neither  $N$  or  $O$  should be directly bound  
 15 to  $Si$ . The value of  $k$  is 0 or 1, the value of  $m$  is from 0 to 20 inclusive, the value of  $n$  is 0, 1 or 2, the value of  $o$  is 0 or 1 and the value of  $p$  is from 0 to 20 inclusive, with the provisos that the sum of the values of  $k$ ,  $m$ ,  $n$ ,  $o$  and  $p$  is at least 1 and not more than 20 and that if  $o$  is 1,  $p$  is 1 or greater and the sum of  $k$ ,  $m$  and  $n$  is 1 or greater, i.e. that the  $Si$  atom is linked directly to a carbon atom. There should be no hydrolysable  
 20 bond between the silicon and nitrogen atoms. Preferably,  $m$  is 3 and 1,  $n$ ,  $o$  and  $p$  are all 0, i.e.,  $R^4$  is  $-CH_2CH_2CH_2-$ .

Without wishing to be bound by any particular theory or mode of action, it is believed that the mechanism of the present process can be illustrated with reference to Figure 2. In the embodiment illustrated in Figure 2, the particulate material being  
 25 treated is silica,  $R^1$ ,  $R^2$  and  $R^3$  are each  $-OCH_3$ ,  $R^4$  is  $-CH_2CH_2CH_2-$ ,  $X$  is  $-Cl$  and the sulfur-containing compound is  $Na_2S_n$ . Thus, in the illustrated embodiment, 3-chloropropyltrimethoxysilane is reacted with the untreated silica particle to produce the illustrated treated particle having a chloropropylsiloxyl moiety (this an example of the particle of Formula II). In the second step, two such treated particles are reacted  
 30 with  $Na_2S_n$  to produce the illustrated coupled particulate material. Thus, as will be apparent to those of skill in the art, while the product of the process in Figure 2 is the same as that in the process of Figure 1, the coupling agent, *per se*, was not produced in

the former. Also, as will be appreciated by those of skill in the art, in the second step, it is possible for the sulfur-containing compound,  $\text{Na}_2\text{S}_n$ , to react with a single silica particle.

In a preferred embodiment the particles have bonded thereto an  
 5 aminohydrocarbonsilane moiety having the formula



in which:

$\text{R}^a$ ,  $\text{R}^b$  and  $\text{R}^c$  are the same or different and each is selected from -O-  
 15 and  
 - $\text{C}_p\text{H}_{2p}$ -, optionally substituted by one or more oxygen atoms and wherein p is an  
 integer of from 1 to 10; and

$\text{R}^{12}$  is a group of formula:



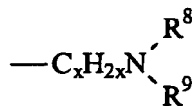
25 or an acid addition or quaternary ammonium salt thereof in which:

$\text{R}^4$  is a divalent group that is resistant to hydrolysis at the Si- $\text{R}^4$  bond;

$\text{R}^5$  is selected from: hydrogen; a  $\text{C}_{1-40}$  alkyl; a  $\text{C}_{2-40}$  mono-, di- or tri-  
 unsaturated alkenyl group; a  $\text{C}_6\text{-C}_{40}$  aryl group; a group of the formula:

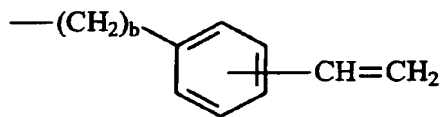


5

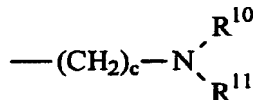


- 10 in which x is an integer from 2 to 10,  $\text{R}^8$  and  $\text{R}^9$ , which may be the same or different, are each selected from: hydrogen;  $\text{C}_{1-18}$  alkyl;  $\text{C}_{2-18}$  mono-, di- or tri-unsaturated alkenyl; phenyl; a group of formula:

15

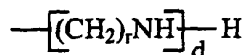


- 20 wherein b is an integer from 1 to 10; a group of formula:



25

- wherein c is an integer from 1 to 10, and  $\text{R}^{10}$  and  $\text{R}^{11}$  may be the same or different and are each selected from: hydrogen,  $\text{C}_{1-10}$  alkyl group or  $\text{C}_{2-10}$  alkenyl group, provided that there is no double bond in the position alpha to the nitrogen atom; and a group of
- 30 formula:



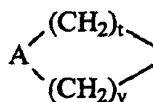
5

wherein r is an integer from 1 to 6 and d is an integer from 1 to 4;

R<sup>6</sup> may be any of the groups defined for R<sup>5</sup> with the provisos that: (i) R<sup>5</sup> and R<sup>6</sup> do not have a tertiary carbon atom adjacent to the nitrogen atom, and (ii) at least one of R<sup>5</sup> and R<sup>6</sup> has a carbon chain at least 8 carbon atoms in length

10  
uninterrupted by any heteroatoms;

or R<sup>5</sup> and R<sup>6</sup> may together form a divalent group of formula:



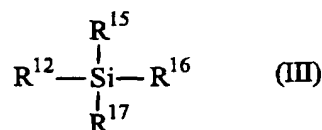
15

in which A is selected from: a -CHR group or a -NR group in which R is hydrogen or a C<sub>6-40</sub> alkyl or C<sub>6-40</sub> alkenyl group, a C<sub>6-40</sub> aryl group, an oxygen atom and a sulfur atom, and t and v are each independently 1, 2, 3 or 4; provided that the sum of t and v does not exceed 6, preferably the sum of t and v is 4.

In copending International patent applications S.N. PCT/CA98/0499 [Koski #1] and S.N. PCT/CA98/0500 [Koski #2], the contents of which are hereby incorporated by reference, there is taught a novel approach for producing masterbatches of polymers and particles. Generally, this approach, as taught in Koski #1, relates to initially rendering the particles hydrophobic to facilitate dispersion thereof in the polymer. Hydrophobicity is conferred to the particles by reacting the particles with a particular aminohydrocarbon silane compound to form the above aminohydrocarbonsilane moiety on the surface of the particles. A particularly preferred process to produce a useful aminohydrocarbon silane compound and a subset of aminohydrocarbon silane compounds are taught in Koski #2. Alternatively, the above aminohydrocarbonsilane moiety can be formed on the surface of the

particles *in situ* using the approach described in Canadian patent application (Bayer Ref: POS-1061) filed on even date herewith, the contents of which are hereby incorporated by reference. If the particle has an aminohydrocarbonsilane moiety formed thereon, it is preferred that the amount of sulfur-containing compound used in the present process is less than the stoichiometric amount necessary to react with substantially all of the pendant reactive groups on the surface of the particles.

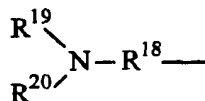
In a preferred embodiment of the present process, the product of the present process is further reacted with a compound of Formula III:



in which:

$\text{R}^{15}$ ,  $\text{R}^{16}$  and  $\text{R}^{17}$  have the same definitions as  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  in Formula I hereinabove; and

$\text{R}^{12}$  is selected from the group comprising a  $\text{C}_{8-40}$  alkyl group or a  $\text{C}_{8-40}$  mono-, di- or tri-unsaturated alkenyl group, either of which can be interrupted by one or more aryl groups, preferably phenyl groups; a group of formula:



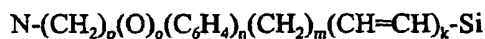
or an acid addition or quaternary ammonium salt thereof in which  $\text{R}^{18}$  is a divalent group resistant to hydrolysis at the Si- $\text{R}^{18}$  bond,  $\text{R}^{19}$  is selected from the group comprising hydrogen, a  $\text{C}_{1-40}$  alkyl group, a  $\text{C}_{2-40}$  mono-, di- or tri-unsaturated alkenyl group, a substituted aromatic group, for example the phenylene group  $-(\text{C}_6\text{H}_4)-$ , the biphenylene Group  $-(\text{C}_6\text{H}_4)-(\text{C}_6\text{H}_4)-$ , the  $-(\text{C}_6\text{H}_4)-\text{O}-(\text{C}_6\text{H}_4)-$  group or the naphthylene group,  $-(\text{C}_{10}\text{H}_6)-$ , the aromatic group being unsubstituted or substituted by a  $\text{C}_{1-20}$  alkyl

or C<sub>2-20</sub> mono-, di- or tri-unsaturated alkenyl group; and R<sup>20</sup> may be any of the groups defined for R<sup>19</sup>, with the provisos that R<sup>19</sup> and R<sup>20</sup> do not have a tertiary carbon atom adjacent to the nitrogen atom and that at least one of R<sup>19</sup> and R<sup>20</sup> has a carbon chain at least 8 carbon atoms in length uninterrupted by any heteroatoms.

- 5 Preferably, R<sup>18</sup> is a C<sub>1</sub>-C<sub>40</sub> saturated or unsaturated group (e.g., alkenyl, aryl, cycloalkyl and the like).

In this preferred embodiment, again, it is preferred that the particulate filler material, more preferably a mineral filler, is in the form of an aqueous slurry or a dispersion, and the compound of Formula III is added to the slurry or dispersion under  
10 intense mixing. In the compound of Formula III the possible and preferred values for R<sup>15</sup>, R<sup>16</sup> and R<sup>17</sup> are the same as the possible and preferred values for R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> that are discussed above in relation to Formula I. If R<sup>12</sup> is an amino group of formula -R<sup>18</sup>-NR<sup>19</sup>R<sup>20</sup>, preferred values for R<sup>18</sup> are such that N-R<sup>18</sup>-Si includes groups of the formula:

15



in which k is 0 or 1, m is 0 to 20 inclusive, n is 0, 1 or 2, o is 0 or 1 and p is 0 to 20 inclusive, provided that the sum of k, m, n, o and p is at least 1 and not greater than  
20 20, and further provided that if o is 1, p is also 1 or greater, and the sum of k, m and n is 1 or greater. The order of the moieties between N and Si is not particularly restricted other than neither N or O should be directly bound to Si. There should be no hydrolysable group between the silicon and nitrogen atoms. Preferably k, n, o and p are all 0 and m is 3, i.e. R<sup>18</sup> is -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-.

- 25 R<sup>12</sup> may be a moiety containing at least one primary, secondary, or tertiary amine nitrogen. In this case the amino group bonded to R<sup>18</sup>- is given by the formula -NR<sup>19</sup>R<sup>20</sup>. R<sup>19</sup> may be a H or a C<sub>1-40</sub> alkyl group or a C<sub>2-40</sub> mono-, di- or tri-unsaturated alkenyl group. R<sup>19</sup> may also be a C<sub>1-20</sub> alkyl-substituted or C<sub>2-20</sub> alkenyl-substituted aromatic group. The aromatic group may be, for example, the phenylene group  
30 -(C<sub>6</sub>H<sub>4</sub>)-, the biphenylene group -(C<sub>6</sub>H<sub>4</sub>)-(C<sub>6</sub>H<sub>4</sub>)-, the -(C<sub>6</sub>H<sub>4</sub>)-O-(C<sub>6</sub>H<sub>4</sub>)- group, or the naphthylene group -(C<sub>10</sub>H<sub>6</sub>)-. R<sup>20</sup> may be one of the same groups as R<sup>19</sup> with the

further proviso that at least one of R<sup>19</sup> and R<sup>20</sup> must contain a continuous carbon chain of at least 8 carbons in length, uninterrupted by any heteroatoms.

As stated above, if R<sup>19</sup> and R<sup>20</sup> are other than hydrogen, the carbon atom attached to the nitrogen atom is not tertiary. Preferably the carbon atom attached to the nitrogen atom is primary, i.e., -CH<sub>2</sub>-.

It is preferred that R<sup>19</sup> is a mono-unsaturated alkenyl group of 12-20 carbons in length and most preferable that R<sup>19</sup> is a monounsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R<sup>20</sup> is H.

Alternatively, R<sup>12</sup> may be a moiety which contains a mineral acid salt or a quaternary ammonium salt of an amine. The formula of R<sup>12</sup> may thus be described by the extended formula -R<sup>18</sup>-NR<sup>19</sup>R<sup>20</sup>·R<sup>21</sup>X wherein -R<sup>18</sup>-, R<sup>19</sup> and R<sup>20</sup> are as previously defined and R<sup>21</sup> may be a H, or a C<sub>1-40</sub> alkyl or C<sub>2-40</sub> mono-, di- or tri-unsaturated alkenyl group and X is an anion, preferably Cl or Br, although sulphate can be used.

If the compound of Formula III is used, there is the further proviso that at least one of R<sup>19</sup> and R<sup>20</sup> must contain a continuous carbon chain of at least 8 carbons in length, uninterrupted by any heteroatom. It is preferred to use an amine salt where R<sup>19</sup> is a mono- or di-unsaturated alkenyl group of 12-20 carbons in length and most preferably that R<sup>19</sup> is a mono- or di-unsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R<sup>20</sup> is H and that R<sup>21</sup> is H and X is chlorine. The preferred hydrophobicizing agent of Formula III is N-oleyl-N-(3-trimethoxysilyl)propyl ammonium chloride.

Preferably, the amount of the hydrophobic compound of Formula III to add is generally between 0.5 and 20 percent by weight of the weight of the particles (preferably mineral particles such as silica) in the slurry (dry basis), and is inversely proportional to the particle size of the silica particles. The compound may be added to the slurry in its natural state, either as a liquid or a solid. However, to facilitate dispersion, it is preferred, where possible, to add the compound as a liquid. If the melting point of the compound is below 95°C, it is preferred to add it to the slurry in a molten state at a temperature at least 5°C above the melting point, provided the temperature of the compound in the liquified state does not exceed 100°C and provided that the compound does not decompose under these conditions. If the melting point exceeds 95°C, it is most preferred to use a solvent. Suitable solvents are

alcohols containing 1 to 5 carbon atoms and most preferably those containing 1 to 3 carbon atoms, that is to say methanol, ethanol, n-propanol or isopropanol. If the compound of Formula III is an alkoxysilane, most preferably the alkoxy group of the solvent alcohol will be the same as the alkoxy group of the alkoxysilane. For  
 5 example, if the compound of Formula III is a methoxysilane, the preferred solvent is methanol. The concentration of the compound in the solvent may be from 10 to 90 percent by weight and most preferably between 25 and 75 percent by weight and most preferably 50 percent by weight. Preferably, the solution is prepared and added to the slurry at a temperature between a lower limit of 0°C and an upper limit which is the  
 10 lower of at least 10°C below the boiling point of the solvent and 95°C.

After the addition of the hydrophobic compound of Formula III which is added, the equivalent balance (EB) should be calculated to determine how much, if any, mineral acid or alkali metal hydroxide (or solutions thereof) to add. The equivalent balance (EB) may be determined from the absolute value of the sum of the  
 15 group values of X, R<sup>15</sup>, R<sup>16</sup> and R<sup>17</sup> and the weight added, and the molecular weight of the compound, according to the following scheme: The group contribution of X for either X=Cl or X=Br is -1, thus if X is present it is given a value of -1. The group contribution of each of R<sup>15</sup>, R<sup>16</sup> and R<sup>17</sup> is generally zero for all groups except as follows: if the group is -CH<sub>3</sub>COO<sup>⊖</sup>, Cl<sup>⊖</sup> or Br<sup>⊖</sup>, in which case it is -1, or if it is amino,  
 20 ONa, OK, or OLi in which case it is +1. If the sum of the group contributions for X, R<sup>15</sup>, R<sup>16</sup> and R<sup>17</sup> is zero, no adjustment with mineral acid or alkali metal hydroxide (or solutions thereof) is necessary. If the sum of the group values is a positive integer, adjustment with mineral acid is desirable, and if it is negative, adjustment with alkali hydroxide is desirable.

25 For example, where R<sup>15</sup>=OC<sub>2</sub>H<sub>5</sub>, R<sup>16</sup>=OCH<sub>3</sub>, R<sup>17</sup>=CH<sub>3</sub> and X=Cl, the sum  $\sum$  of the group values (g.v.) is:

$$\sum = (\text{g.v. OC}_2\text{H}_5) + (\text{g.v. OCH}_3) + (\text{g.v. CH}_3) + (\text{g.v. Cl}) = (0) + (0) + (0) + (-1) = -1.$$

30 The negative sign in front of the sum indicates adjustment with alkali metal hydroxide is required. The number of equivalents of alkali required is given by the

equivalent balance (EB) which includes the absolute value of the sum of the group contributions ( $|\sum|$ ) as a scaling factor.

$$EB = \frac{|\sum| \times \text{weight in grams of the compound added}}{\text{molecular weight of the added chemical.}}$$

In continuing the example, if a process according to the present invention were scaled so as to require 3450 grams of a compound of Formula III with a molecular weight of 466 grams and the sum of the group values gave -1, EB would be calculated as follows:

$$EB = |-1| \times 3450/466 = 7.4 \text{ gram-equivalents.}$$

Thus, in this example, 7.4 gram-equivalents of alkali metal hydroxide would be added. Sodium hydroxide is the preferred alkali metal hydroxide. The weight of sodium hydroxide added would be:

$$\text{Weight} = (EB) \times (\text{Equivalent Weight of NaOH}) = 7.4 \times 40.0 = 296 \text{ grams.}$$

The preferred technique according to the invention is to dissolve the alkali hydroxide or mineral acid in water so as to obtain a concentration between 5 and 25% by weight and most preferably between 5 and 10% by weight prior to adding the solution to the slurry. The temperature of the solution may be from 0° to 100°C under atmospheric pressure, or if a pressure vessel is used for preparation of the solution, it may be from 0° to 130°C. It is preferred that the temperature of the solution be within 10°C of the solution of the slurry. The dispersion of the solution in the slurry is effected by mixing.

The product of this preferred embodiment of the present process described thus far relates an aqueous slurry or dispersion of hydrophobicized particles (i.e., it has not yet been contacted with a polymer or other substrate to be filled), which can be used as such or can be filtered and dried.

The hydrophobicized particles may be used as a compounding agent in a multitude of materials including, but not limited to, the following: polymers, alkyd

paints, toners such as those used in photocopiers, modified plastics and rubber vulcanizates.

In a preferred embodiment of this invention the hydrophobicized particles, in the aqueous dispersion or slurry, is incorporated into a polymer, for example an elastomer to form a rubber masterbatch. The slurry is mixed with a hydrocarbon or other solution of the elastomer. Preferably, the solvent in which the elastomer is dissolved is immiscible with, or mostly immiscible with, water to form a preblend. This elastomer solution may be made by dissolving the solid elastomer in a solvent, or it may be the solution resulting from the polymerisation of monomers in the solvent.

The elastomer may be a hydrocarbon rubber, a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation. Other suitable polymers include, but are not limited to butyl rubber (IIR), halogenated butyl rubber (HIIR), cis-1,4-polyisoprene rubber (IR), ethylene-propylene-diene monomer (EPDM) rubber, ethylene-propylene monomer (EPM) rubber, styrene-butadiene rubber (SBR), polybutadiene rubber (BR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), HSRE, natural rubber (NR), polystyrene (PS), chloroprene<sup>1</sup> rubber (CR), ethylene-vinyl acetate (EVM) rubber, epichlorohydrin (ECO) rubber, chlorinated polyethylene, silicone rubber (Q), urethane rubber (AU-EU), acrylonitrile-butadiene-styrene (ABS) polymers and the like. Suitable solvents include but are not limited to cyclohexane, hexane, benzene, toluene and pentane. Optionally, processing oil and antioxidants may be added to the hydrocarbon solution prior to mixing with the slurry, or they may be added after mixing the slurry and the elastomer solution.

The viscosity of the final elastomer solution, sometimes referred to as an elastomer cement, containing the optional ingredients is preferably such that it closely matches the viscosity of the silica slurry and is generally between 1,000 and 50,000 centipoise. The temperature of the elastomer solution is preferably the same as that of the slurry and the amount of cement that is added is such that the final masterbatch may contain from 5 to 250 parts of silica per hundred parts of elastomer, preferably

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<sup>1</sup>Also known as Neoprene™.



from 35 to 100 parts of silica per hundred parts of elastomer, most preferably from 60 to 80 parts of silica per hundred parts of elastomer.

The elastomer cement and, optionally, oil and antioxidants, is mixed with the silica slurry until the mixture becomes homogeneous and the milky colour of the silica  
5 slurry disappears to form a preblend. A small amount of water may separate at this stage.

If not added previously, or if additional amounts are desired, oil and antioxidants may be added next and the mixing continued further until the oil and antioxidant become incorporated in the continuous phase.

10 Any water which separates from the preblend may be removed, discarded or recycled for silica slurry make-up by stopping the agitator for a suitable period and allowing the water phase to accumulate in the bottom of the mixing tank from which it may be drained prior to proceeding with the next step. Agitation is preferably restarted after the water layer is removed.

15 If antioxidants and processing oil were not previously added, or if additional amounts are desired, they may be added at this stage and stirring continued until the preblend is again homogeneous.

The preblend is then added to water heated to a temperature equal to, or preferably higher than the boiling point of the solvent used for the elastomer cement  
20 so as to remove the solvent and produce a masterbatch coagulum in the form of a crumb suspended in water. The preferable temperature of the water prior to addition of the preblend is between 50° and 100°C, most preferably between 90° and 95°C, and the preblend is added at a rate so as to maintain a so-fixed or reasonably so-fixed water temperature throughout the coagulation. The agitation is set sufficiently high so  
25 as to maintain the crumb in a suspended state within the water but not so high as to cause the crumb to subdivide into particles smaller than approximately 5 millimeters.

The solvent may be recovered from the coagulator by recondensing the vapours. The material containing the suspended crumb is passed through a filter screen sized so as to recover the wet masterbatch. The material passing through the  
30 screen may be optionally recycled for further silica slurry make-up.

The wet crumb is dried such as by using forced air or fluidized bed or microwave drying techniques at a temperature between about 75° and about 135°C,

preferably between about 85° and about 120°C, most preferably between about 85° and about 105°C, until a suitably dry masterbatch crumb is obtained.

The dried crumb may be further processed according to industry and customer requirements.

5           Another advantageous application of the hydrophobicized particles is in the production of predispersions or concentrates of polymer compounding chemicals. These materials typical include a chemical of interest which is predispersed in high concentrations (at least about 50 percent by weight as discussed hereinabove) in a binder, preferably a polymeric material, and are supplied in the form of pellets, slabs  
10 and the like. Thus, the polymer acts as a binder for the chemical of interest. The chemical of interest may, for example, be a silica filler, a colorant, a pigment, an inorganic activator, a stabilizer and/or a flame retardant for use to produce a polymer-based product.

          In a preferred embodiment of this invention the hydrophobicized particles, in  
15 the aqueous dispersion or slurry, are incorporated into a binder material, for example a polymer in the form of a polymer solution or cement. The slurry of treated particles is mixed with a hydrocarbon or other non-aqueous solution of the binder. Preferably, the solvent in which the binder is dissolved is immiscible with, or mostly immiscible with, water to form a preblend. This binder solution (e.g., polymer cement) may be  
20 made by dissolving the solid polymer in a solvent or, in the case of a solution polymer, it may be the solution resulting from the polymerisation of monomers in the solvent.

          Preferably, the binder is a polymer. It will, however, be appreciated by those of skill in the art that the binder may be a quasi- or non-polymeric material such as a  
25 polyethylene wax, a rosin, a fatty acid, a high molecular weight liquid and the like, or a combination of polymer and such quasi- or non-polymeric material.

          The polymer may be an elastomer (e.g., a hydrocarbon rubber), a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation, a plastic and the like.

30           Elastomers are well known to those of skill in the art. Non-limiting examples of suitable elastomers may be selected from the group comprising natural rubber (NR), depolymerized NR, cis-1,4-polyisoprene rubber (IR), polybutadiene rubber

(BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), butyl rubber (IIR), halogenated butyl rubber (HIIR), ethylene-propylene monomer (EPM) rubber, ethylene-propylene-diene monomer (EPDM) rubber, chloroprene rubber (CR), ethylene-vinyl acetate (EVM) rubber, silicone rubber (Q), epichlorohydrin (ECO) rubber, urethane rubber (AU EU) and the like.

Plastics are well known to those of skill in the art. Non-limiting examples of suitable plastics may be selected from the group comprising polystyrene, polyethylene, polypropylene, chlorinated polyethylene, acrylonitrile-butadiene-styrene (ABS) polymers, ethylene-vinyl-acetate (EVA) pastic, polyvinyl chloride (PVC), plasticized polyvinyl chloride (PVC), polymethylmethacrylate (PMMA), epichlorohydrin (ECO) plastic and the like.

Of course those of skill in the art will recognize and appreciate that the foregoing materials may be modified with respect to parameters such as monomer sequence, monomer ratio, molecular weight ( $M_n$ ,  $M_w$ , etc.), molecular weight ratio and the like while still being useful in the present invention.

The selection of a suitable solvent for preparation of the polymer binder solution is within the purview of a person skilled in the art and depends on the specific polymer to be dissolved. Non-limiting examples of suitable solvents may be selected from the group comprising cyclohexane, chlorobenzene, hexane, benzene, toluene, pentane and the like. Optionally, processing oil, antioxidants and other chemicals known in the art as processing aids may be added to the hydrocarbon solution prior to mixing with the slurry, or they may be added after mixing the slurry and the polymer solution.

The viscosity of the final polymer solution, sometimes referred to as a polymer cement, containing the optional ingredients, is preferably such that it closely matches the viscosity of the slurry of treated particles and is generally between 1,000 and 50,000 centipoise. This may depend, at least in part on the specific gravity and/or particle size of the particles dispersed in the slurry. The temperature of the polymer solution is preferably the same as that of the slurry. Further, it is preferred to add the polymer cement in an amount such that the final dried dispersion may contain the treated particulate material as the major component of the composition - i.e., the

dispersion comprises at least about 50 percent by weight particulate material. Preferably, the dispersion comprises from about 50 to about 95, more preferably from about 60 to about 95, even more preferably from about 70 to about 95, percent by weight particulate material.

5        The polymer cement and, optionally, oil and antioxidants, is mixed with the slurry of treated particles until the mixture becomes homogeneous. This is confirmed by assessing the uniformity of colour and/or solids dissolution (i.e., the present of a substantially single phase although a small insubstantial amount of water may separate at this stage).

10       If not added previously, or if additional amounts are desired, oil and antioxidants may be added next and the mixing continued further until the oil and antioxidant become incorporated in the continuous phase.

Any water which separates from the preblend may be removed, discarded or recycled for slurry make-up by stopping the agitator for a suitable period and allowing  
15       the water phase to separate in the mixing tank from which it may be removed prior to proceeding with the next step. Agitation is preferably restarted after the water layer is removed.

If antioxidants and processing oil were not previously added, or if additional amounts are desired, they may be added at this stage and stirred to disperse them.

20       The preblend is then added to water heated to a temperature equal to, or preferably higher than the boiling point of the solvent used for the polymer cement so as to remove the solvent and produce a dispersion coagulum in the form of a crumb suspended in water. Preferably, the temperature of the water prior to addition of the preblend is in the range of from about 50°C to about 100°C, more preferably in the  
25       range of from about 90°C and to about 95°C. Further, it is preferred to add the preblend at a rate so as to maintain a temperature substantially within thereof preferred ranges. The agitation is set sufficiently high so as to maintain the crumb in a suspended state within the water, but not so high as to cause the crumb to subdivide into particles smaller than approximately 5 mm.

30       The solvent may be recovered from the coagulator by condensing the vapours. The material containing the suspended crumb may then be passed through a filter

screen sized so as to recover the wet composition. The filtrate from this step may be optionally recycled for further slurry make-up.

The wet crumb is dried such as by using forced air or fluidized bed or microwave or other drying techniques. If microwave or other drying techniques are used, it is preferred to conduct these at a temperature in the range of from about 75°C to about 135°C, preferably in the range of from about 85°C to about 120°C, most preferably in the range of from about 85°C to about 105°C, until a suitably dry dispersion crumb is obtained.

The dried crumb may be further processed according to industry and customer requirements.

Embodiments of the present invention will be illustrated with reference to the following Examples which should not be used to construe or limit the scope of the invention.

**Example 1**

In this Example, the following materials were used:

Hi-Sil™ 233

triethoxysilane

chloroplatinic acid

allyl bromide

sodium tetrasulfide

oleylamine

Buna™ CB-24 (polybutadiene) cement in hexane

Sundex™ 8125

Vulcanox™ 4020

N-oleyl-N-(trimethoxysilyl) propyl ammonium chloride

In a 4 L glass beaker in a fumehood were combined 510 grams of Hi-Sil™ 233 (amorphous precipitated silica) and 2040 grams of water, and the resulting mixture was stirred with an air-driven stirrer equipped with a radial impeller until a smooth

slurry was obtained. The beaker was placed on a hot plate and the slurry was heated to 60°C while under high agitation.

Triethoxysilane (40.0 grams, 240 millimoles) was added into the vortex dropwise over 5 minutes. After 10 minutes of stirring, allyl bromide (25.0 grams, 207 millimoles) was added dropwise to the stirring slurry. Using a pipette, 5.0 mL of an 0.5% solution of chloroplatinic acid in methanol were added to the beaker. After 2 hours of additional stirring at 59-60°C, commercial aqueous sodium tetrasulfide solution (38.8 grams of 34 wt% Na<sub>2</sub>S<sub>4</sub>) was added in one shot. The slurry immediately turned a greenish-grey colour. The viscosity increased somewhat and then decreased after 5 minutes. The agitator power was adjusted to maintain circulation.

After two hours and twenty minutes of additional stirring, the colour had faded to an off-white. The agitation was shut off and the beaker was removed from the heat source. The slurry was covered with plastic wrap and allowed to sit overnight in a quiescent state at room temperature. The following morning, the material in the beaker was again placed under agitation at room temperature. A check of the pH using a pH meter gave a reading of 8.4. Commercial distilled oleylamine (Akzo ARMEEN OLD, 14.6 grams, ~55 millimoles) was dissolved in 50 mL of methanol and the resulting solution was added to the vortex over 5 minutes in 1 mL aliquots. Heating was commenced and the slurry was kept between 40° and 50°C for two hours. The pH fell steadily during this period from an initial 8.8 to a final 8.5. The pH was then adjusted to 7.5 with diluted hydrochloric acid.

The slurry was cooled to room temperature and then transferred quantitatively to 2.5 L plastic bucket in a fumehood by use of a spatula and a small amount (~55 mL) of wash water.

Polybutadiene cement (3188 grams of 20 wt% Buna™ CB-24 in hexane), Sundex™ 8125 aromatic process oil (191 grams) and Vulcanox™ 4020 antioxidant (5.0 grams) were then added. The blend was agitated manually for 5 minutes with a spatula. The blend was then placed under agitation using the air stirrer an impeller combination used previously. After several minutes, most of the treated silica was picked up by the organic phase and a small volume of cloudy water separate. N-Oleyl-N-(trimethoxysilyl)propyl ammonium chloride (9.6 grams of 50 wt% solution

in methanol) was then added to the water phase and mixing was continued for several minutes to yield a crystal clear water phase.

Coagulating was done in a fume hood to remove the solvent. The blend was added slowly to stirred water maintained at 92-95°C with low pressure steam. The aqueous coagulation serum remained clear throughout the coagulation. The wet crumb was isolated by screening through a 1-mm sieve, water washed and then dried for 4 hours at 85°C. Product yield was 1327 grams, dry basis.

#### Example 2

10 In this Example, the following materials were used.

Hi-Sil™ 233

3-chloropropyltrimethoxysilane

sodium tetrasulfide

15 oleylamine

Buna™ CB-24 (polybutadiene) cement in hexane

Sundex™ 8125

Vulcanox™ 4020

20 In a 4 L glass beaker in a fumehood were combined 510 grams of Hi-Sil 233 (amorphous precipitated silica) and 2040 grams of water and the resulting mixture was stirred with an electrically driven stirrer equipped with a radial impeller until a smooth slurry was obtained. The beaker was placed on a hot plate and the slurry was heated to 70°C while under high agitation.

25 3-Chloropropyltrimethoxysilane (41.0 gm, 206 millimoles) was added to the vortex dropwise over 10 minutes and stirring was continued for 30 minutes. Commercial distilled oleylamine (Akzo ARMEEN OLD, 1.43 grams, ~5.3 millimoles) was added to the vortex dropwise over 10 minutes. Stirring was continued for an additional 15 minutes. Sodium hydroxide solution (0.22 grams in 10 mL water) was then added dropwise to the vortex over 5 minutes. The slurry viscosity increased markedly but the material was still mobile.

The above slurry was then heated to 80°C while agitation was maintained. Sodium tetrasulfide solution (38.8 grams of 34 wt% Na<sub>2</sub>S<sub>4</sub> in water) was then added over 10 minutes. The colour gradually deepened from a dark yellow to a Kelly green. The slurry was stirred for an additional 4 hours at between 80-85°C. When the slurry became too thick for good agitation, additional water was added as required to enable circulation to be maintained. Slurry volume was maintained at around 2500 mL. The total water added was 900 mL over the 4 hour period. After the end of the period the slurry have returned to a white colour. Commercial distilled oleylamine (Akzo ARMEEN OLD, 13.2 grams, ~49.4 millimoles) was then added dropwise to the vortex over 10 minutes. Stirring was continued for 30 minutes after the end of the amine addition. Sodium hydroxide solution (2.0 grams in 50 mL of water) was then added dropwise to the vortex over 10 minutes. Considerable thickening of the slurry was evidenced. The heat source was then removed and the slurry was allowed to cool to ambient under slow agitation. The pH of the final slurry was 8.5

When cool, the cement was quantitatively transferred to a 2,5 gallon plastic bucket in the fume hood by using a spatula and a small amount (~50 mL) of water from a wash bottle. Polybutadiene cement (3984 grams of 16 wt% Buna™ CB-24 hexane), Sundex™ 8125 aromatic process oil (191 grams) and Vulcanox™ 4020 antioxidant (5.0 grams) were then added and the mixture was stirred manually with a spatula to homogenize.

Homogenization was continued with an air stirrer for an additional 5 minutes. The mixture became extremely viscous and elastic during this time. Small beads of water which separated were crystal clear.

Coagulating to remove the solvent was done in a fumehood. The blend was added slowly to stirred water which was maintained at 92-95°C using low pressure steam. The aqueous coagulation serum remained almost clear throughout the coagulation although some foaming was experienced. The wet crumb was isolated by screening through a 1-mm sieve, water washed and then dried for 4 hours at 85 degrees Celsius. Product yield was 1263 grams, dry basis.

While the present invention has been described with reference to preferred embodiments and illustrative Examples, it will of course be understood by those of



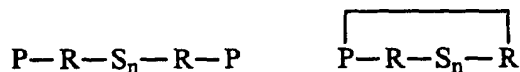
skill in the art that various modifications to these preferred embodiment and illustrative Examples may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for treating particles, the process comprising the step of:  
contacting a particulate material having Formula II:

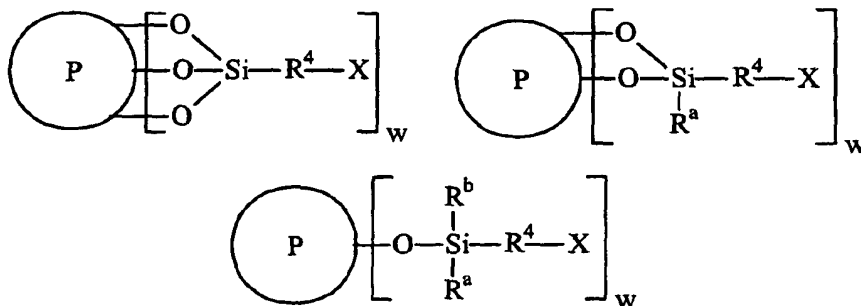


wherein P is a particle, R is a hydrocarbylsiloxy moiety and X is an anion, with a sulfur-containing compound to produce a particulate material having one or more of the formulae:



wherein n is an integer from 1 to 10.

2. The process defined in claim 1, wherein n is an integer of from 2 to 5.
3. The process defined in any one of claims 1-2, wherein the particles of Formula II are selected from the group comprising:



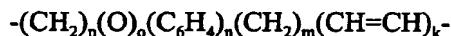
wherein:

$R^4$  is a divalent group that is resistant to hydrolysis at the Si- $R^4$  bond;

$R^a$  and  $R^b$  are the same or different and each is selected from the group comprising hydroxyl, a hydrolysable group,  $C_{1-40}$  alkyl,  $C_{2-40}$  mono- or diunsaturated alkenyl and  $C_{3-40}$  aromatic;

w is an integer in range of 1 to  $10^6$  or more.

4. The process defined in claim 3, wherein  $R^4$  has the formula:



wherein the order of the moieties is not restricted and

k is 0 or 1,

m is a whole number in the range 0 to 20,

n is 0, 1 or 2,

o is 0 or 1, and

p is a whole number in the range 0 to 20,

with the provisos that: (i) the sum of the values of k, m, n, o and p is at least 1 and not more than 20, and (ii) if o is 1, p is 1 or greater and the sum of k, m and n is 1 or greater.

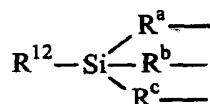
5. The process defined in claim 3, wherein  $R^4$  is  $-CH_2CH_2CH_2-$ .

6. The process defined in claim 3, wherein X is selected from the group comprising acetate, chloride, bromide, iodide and sulphate.

7. The process defined in claim 3, wherein X is selected from the group comprising chloride and bromide.

8. The process defined in any one of claims 1-7, wherein the sulfur-containing compound is selected from the group comprising sulfides, thiosulfates and mixtures thereof.

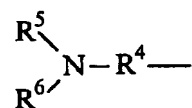
9. The process defined in claim 8, wherein the sulfides comprise ammonium sulfide compounds and alkali metal sulfide compounds.
10. The process defined in claim 9, wherein the alkali metal sulfide comprises  $\text{Na}_2\text{S}_n$ ,  $\text{K}_2\text{S}_n$  and mixtures thereof, and n is as defined above.
11. The process defined in claim 8, wherein the thiosulfates comprise ammonium thiosulfate compounds and alkali metal thiosulfate compounds.
12. The process defined in claim 11, wherein the alkali metal thiosulfate compound comprises  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{K}_2\text{S}_2\text{O}_3$  and mixtures thereof, and n is as defined above.
13. The process defined in any one of claims 1-12, wherein the reaction is conducted in an aqueous medium.
14. The process defined in any one of claims 1-13, wherein the particles have bonded thereto an aminohydrocarbonsilane moiety having the formula



in which:

$\text{R}^a$ ,  $\text{R}^b$  and  $\text{R}^c$  are the same or different and each is selected from -O- and  $-\text{C}_p\text{H}_{2p}-$ , optionally substituted by one or more oxygen atoms and wherein p is an integer of from 1 to 10; and

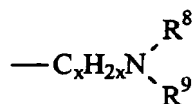
$\text{R}^{12}$  is a group of formula:



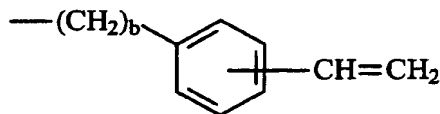
or an acid addition or quaternary ammonium salt thereof in which:

$\text{R}^4$  is a divalent group that is resistant to hydrolysis at the  $\text{Si-R}^4$  bond;

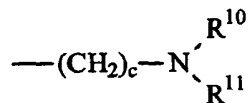
$\text{R}^5$  is selected from: hydrogen; a  $\text{C}_{1-40}$  alkyl; a  $\text{C}_{2-40}$  mono-, di- or tri-unsaturated alkenyl group; a  $\text{C}_6\text{-C}_{40}$  aryl group; a group of the formula:



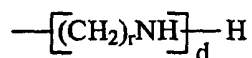
in which x is an integer from 2 to 10,  $\text{R}^8$  and  $\text{R}^9$ , which may be the same or different, are each selected from: hydrogen;  $\text{C}_{1-18}$  alkyl;  $\text{C}_{2-18}$  mono-, di- or tri-unsaturated alkenyl; phenyl; a group of formula:



wherein b is an integer from 1 to 10; a group of formula:



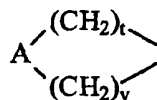
wherein  $c$  is an integer from 1 to 10, and  $\text{R}^{10}$  and  $\text{R}^{11}$  may be the same or different and are each selected from: hydrogen,  $\text{C}_{1-10}$  alkyl group or  $\text{C}_{2-10}$  alkenyl group, provided that there is no double bond in the position alpha to the nitrogen atom; and a group of formula:



wherein  $r$  is an integer from 1 to 6 and  $d$  is an integer from 1 to 4;

$\text{R}^6$  may be any of the groups defined for  $\text{R}^5$  with the provisos that (i)  $\text{R}^5$  and  $\text{R}^6$  do not have a tertiary carbon atom adjacent to the nitrogen atom, and (ii) at least one of  $\text{R}^5$  and  $\text{R}^6$  has a carbon chain at least 8 carbon atoms in length uninterrupted by any heteroatoms;

or  $\text{R}^5$  and  $\text{R}^6$  may together form a divalent group of formula:



in which A is selected from: a  $-\text{CHR}$  group or a  $-\text{NR}$  group in which R is hydrogen or a  $\text{C}_{6-40}$  alkyl or  $\text{C}_{6-40}$  alkenyl group, a  $\text{C}_6\text{-C}_{40}$  aryl group, an oxygen atom and a sulfur atom, and  $t$  and  $v$  are each independently 1, 2, 3 or 4; provided that the sum of  $t$  and  $v$  does not exceed 6.

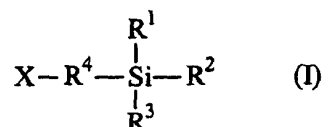
15. The process defined in any one of claims 1-14, wherein the particles comprise inorganic water insoluble compounds.
16. The process defined in any one of claims 1-15, wherein the particles comprise silica.
17. The process defined in any one of claims 1-15, wherein the particles are selected from the group consisting of titanium oxide, ferric oxide, hydrated ferric oxide, ferrous oxide, antimony oxide, barium carbonate, zinc oxide, zinc borate, lead oxide (including red lead oxide), dibasic lead phosphite, lead silicate, tribasic lead sulfate and mixtures thereof.
18. The process defined in any one of claims 1-17, comprising the further step of: admixing the treated particles with a polymer solution and forming the mixture into a polymer dispersion.
19. The process defined in any one of claims 1-17, comprising the further step of: admixing a slurry of treated particles with a polymer solution and forming the mixture into a polymer dispersion.
20. The process defined in any one of claims 18-19, wherein the polymer solution comprises a polymer and a solvent.
21. The process defined in any one of claims 18-20, wherein the polymer is selected from the group consisting of an elastomer, a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation, a plastic and mixtures thereof.
22. The process defined in claim 21, wherein the elastomer is selected from the group consisting of natural rubber (NR), cis-1,4-polyisoprene rubber (IR), polybutadiene rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), butyl rubber

(IIR), halogenated butyl rubber (HIIR), ethylene-propylene monomer (EPM) rubber, ethylene-propylene-diene monomer (EPDM) rubber, chloroprene rubber (CR), ethylene-vinyl acetate (EVM) rubber, silicone rubber (Q), epichlorohydrin (ECO) rubber, urethane rubber (AU EU) and mixtures thereof.

23. The process defined in claim 21, wherein the plastic is selected from the group consisting of polystyrene, polyethylene, polypropylene, chlorinated polyethylene, acrylonitrile-butadiene-styrene (ABS) polymers, ethylene-vinyl-acetate (EVA) plastic, polyvinyl chloride (PVC), plasticized polyvinyl chloride (PVC), polymethylmethacrylate (PMMA), epichlorohydrin (ECO) plastic and mixtures thereof.

24. A process for treating particles, the process comprising the steps of:

- (i) contacting a particulate material with a compound of Formula I:



in which:

at least one of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are hydroxyl or hydrolysable groups;

$\text{R}^4$  is a divalent group that is resistant to hydrolysis at the  $\text{Si}-\text{R}^4$  bond; and

X is an anion; and

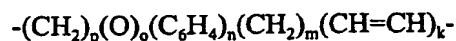
- (ii) contacting the particulate material with with a sulfur-containing compound.

25. The process defined in claim 24, wherein each of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  is hydroxyl or a hydrolysable group.

26. The process defined in any one of claims 24-25, wherein the hydrolysable group has the formula  $-\text{OC}_p\text{H}_{2p+1}$ , where p has a value from 1 to 10.



27. The process defined in any one of claims 22-26, wherein  $R^4$  has the formula:



wherein the order of the moieties is not restricted and

k is 0 or 1,

m is a whole number in the range 0 to 20,

n is 0, 1 or 2,

o is 0 or 1, and

p is a whole number in the range 0 to 20,

with the provisos that: (i) the sum of the values of k, m, n, o and p is at least 1 and not more than 20, and (ii) if o is 1, p is 1 or greater and the sum of k, m and n is 1 or greater.

28. The process defined in any one of claims 22-27, wherein X is selected from the group comprising acetate, chloride, bromide, iodide and sulphate.

29. The process defined in any one of claims 22-27, wherein X is selected from the group comprising chloride and bromide.

30. The process defined in any one of claims 22-29, wherein the sulfur-containing compound is selected from the group comprising sulfides, thiosulfates and mixtures thereof.

31. The process defined in claim 30, wherein the sulfides comprise ammonium sulfide compounds and alkali metal sulfide compounds.

32. The process defined in claim 31, wherein the alkali metal sulfide comprises  $Na_2S_n$ ,  $K_2S_n$  and mixtures thereof, wherein n is as defined above.

33. The process defined in claim 30, wherein the thiosulfates comprise ammonium thiosulfate compounds and alkali metal thiosulfate compounds.

34. The process defined in claim 33, wherein the alkali metal thiosulfate compound comprises  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{K}_2\text{S}_2\text{O}_3$  and mixtures thereof, wherein n is as defined above.

35. The process defined in any one of claims 22-34, wherein the reaction is conducted in an aqueous medium.

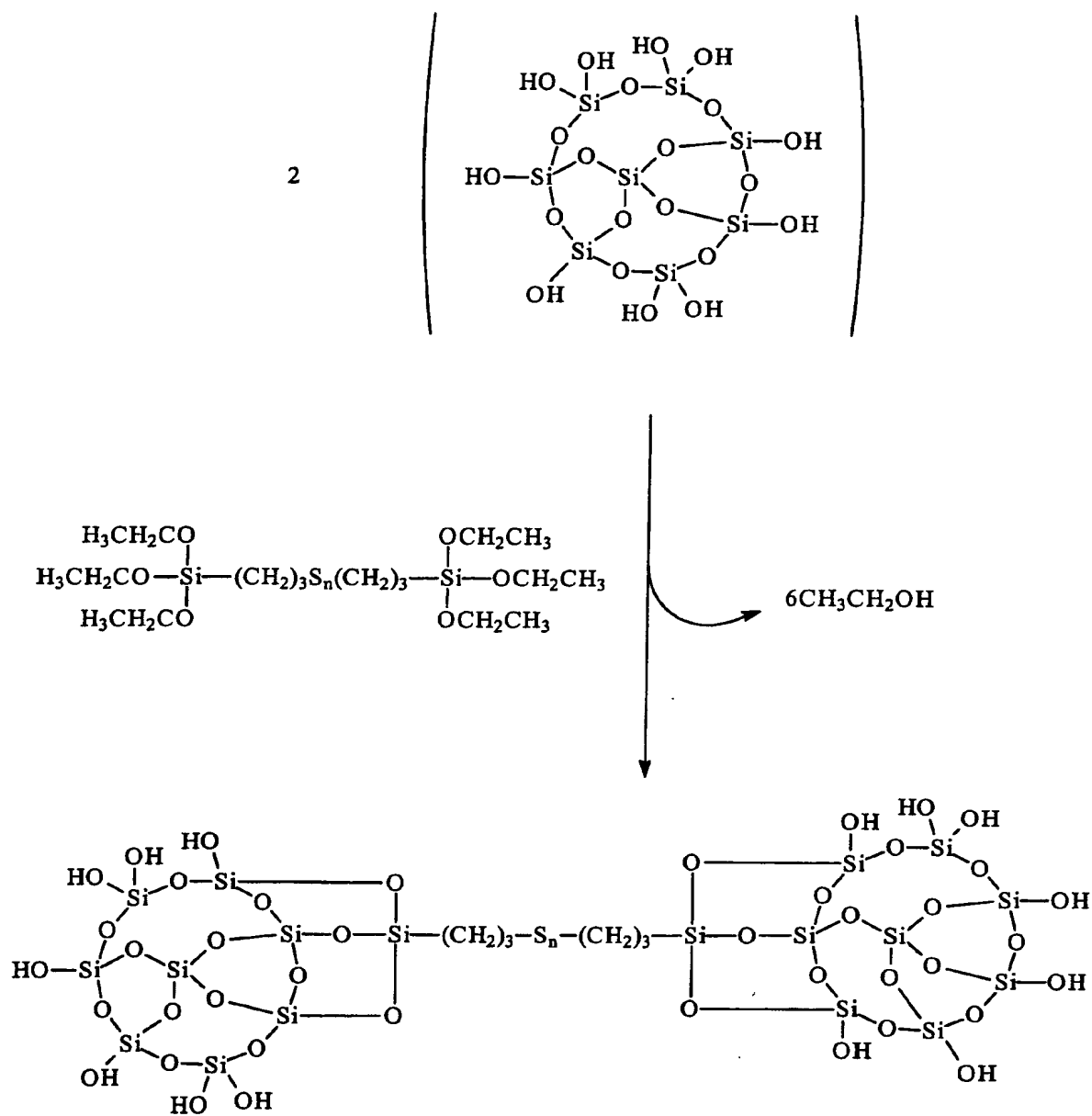


FIG. 1

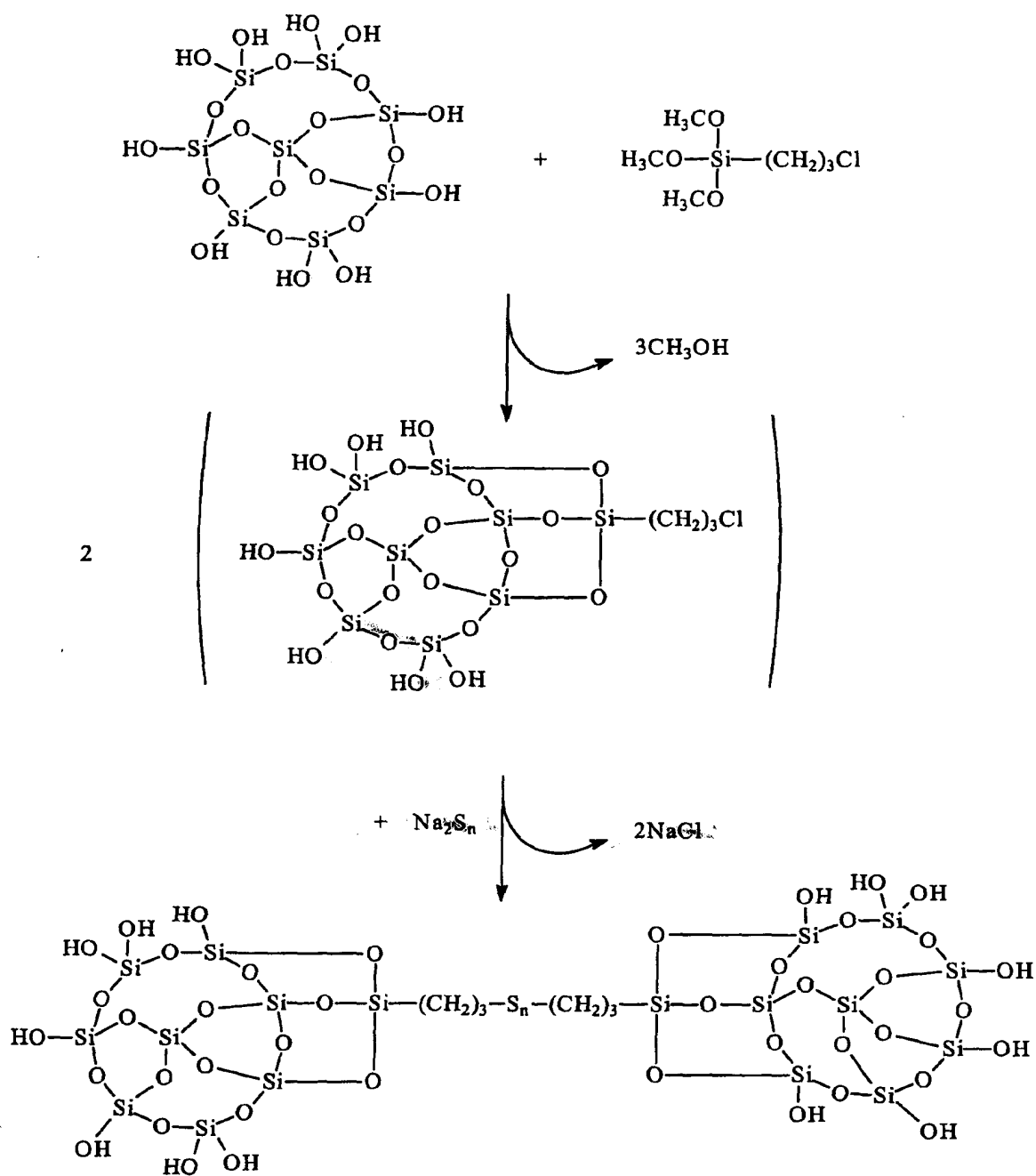


FIG. 2